Northop Grumman CSIA Data. 04-12-16

When CSIA is performed for 1,4-D on a sample, 1,4-D is extracted from water samples using Solid Phase Extraction tubes (Munch and Grimmett, EPA Method 522). Solvent (dichloromethane, DCM) eluted 1,4-D is concentrated before introduction into the GC injection port. After separation of the VOCs on the GC column the eluting gas flow is oxidized (for carbon measurements) or pyrolyzed (for hydrogen measurements) and the resulting gas stream of either CO_2 in helium or H_2 In helium is ready for isotope analysis in the IRMS (EPA Guidance on CSIA, Dec. 2008).

RESULTS AND DISCUSSION

Six groundwater samples with detectable TCE and/or 1,4-D were received for this initial CSIA study. Sampling locations and parameters for CSIA forensics are displayed in **Figure 1**. The concentrations of 1,4-D and VOCs were measured by Method EPA 522 & SW846 8260B, respectively and are shown in **Table 1,** below. Note that "Pace CSIA Lab ID" and "Client Sample ID" are rearranged in **Table 1** according to the natural groundwater flow path, which is towards the south-southeast.

Table 1 Concentrations of 1,4-D and select VOC contaminants in samples from the GABF site

Pace CSIA Lab ID	Client Sample ID	Concentrations of Contaminants (µg/L)							
		1,4-D	VC	cDCE	TCE	PCE	11DCA	111TCA	Freon-113
18242-2	BCP MW-4-1	116	390	390	99	1.5	18	4.6	<1
18233-2	GM73D2	7.6	<1	<1	33	1.4	<1	<1	<1
18242-1	RE122D1	12.9	<1	1.8	590	1.5	<1	<1	4.3
18233-1	TT101D2	4.1	<1	2.0	590	<1	<1	<1	19
18232-2	BPOW3-4	3	<1	<1	73	<1	<1	<1	<1
18232-1	BPOW3-2	6	<1	<1	<1	<1	<1	<1	<1

As seen in **Table 1**, contaminants were detected in the highest concentrations at locations between the presumed upgradient well, BCP MW-4-1 and the presumed downgradient well, TT101D2. TCE in well BCP MW-4-1 (99 µg/L) is being biodegraded into its daughter products cDCE (390µg/L) and then VC (390 µg/L). However, these daughter products of TCE were nearly absent in the two down gradient wells RE122D1 and TT101D2 (<1-2 µg/L). Other VOCs [e.g., 1,1,1-trichloroethane (111TCA) and 1,1-dichloroethane (11DCA)] were present in the well BCP MW-4-1, but were not detectable in the downgradient wells. Freon-113 was detected in the two downgradient wells RE122D1 and TT101D2 (at 4.3 and 19 µg/L, respectively) but not in the upgradient well.

1,4-D was often used as a stabilizer in 111TCA. 111TCA can be degraded through a variety of mechanisms, some biologic (Egli, et al., 1987; Galli, et al., 1989) and some abiotic (Gerkens, et al., 1989).

While 1,4-D degradation has been observed at some sites, 1,4-D is much more recalcitrant than 111TCA (Mohr, et al., 2010). Thus, the 111TCA can degrade while the 1,4-D persists, and this could lead to the appearance of the 1,4-D in downgradient wells where there has been no measureable 111TCA. Alternately, 1,4-D is often found as an impurity in de-icing fluids, so its presence may not coincide with 111TCA. In addition, 1,4-D is completely water miscible and can migrate faster in groundwater than its associated parent plume (Mohr et al., 2010).

As shown in **Table 1**, except for the upgradient well BCP MW-4-1 (with 1,4-Ddetected at 116 µg/L), the 1,4-D detected in the other five monitoring wells at the GABF site was either close to or below 10 µg/L. 1,4-D was detected along with TCE in the downgradient well BPOW3-4, while in the further downgradient well BPOW3-2, only 1,4-D was detected.

CSIA Results from the GABF Site

Results of the $\delta^{13}C$ and $\delta^{37}Cl$ of TCE and the $\delta^{13}C$ and $\delta^{2}H$ of 1,4-D are illustrated in **Table 2** and **Table 3**, respectively. Isotope ratios for certain samples could not be determined (labeled as ND) because the concentration of the target compound was too low to ensure reliable isotopic results. Standard precisions of CSIA for carbon and chlorine isotopes are both at ±0.50‰ (in PDB and SMOC, respectively). For compounds giving low signals, the errors increase. Precisions for such carbon and chlorine isotope analyses will be up to ±2‰ (in PDB and SMOC, respectively) and labeled with a J flag. Standard precision of CSIA for hydrogen isotopes is at ±5‰ (in SMOW). For compounds giving low signals, the errors increase. Precisions for such hydrogen isotope analyses will be up to ±20‰ (in SMOW) and labeled with a J flag.

Table 2 CSIA Results obtained for TCE in 6 samples from the GABF site

Pace Lab ID	Client Sample ID	Concentrations (µg/L)	$\delta^{13}C$ (‰ PDB)	$\delta^{37}Cl$ (‰ SMOC)
18242-2	BCP MW-4-1	99	-21.13	-0.54
18233-2	GM73D2	33	-24.44	-2.75
18242-1	RE122D1	590	-23.90	-2.74
18233-1	TT101D2	590	-24.55	-2.63
18232-2	BPOW3-4	73	-22.62	-1.92
18232-1	BPOW3-2	<1	N/A	N/A